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# PATENT SPECIFICATION

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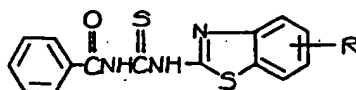
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## (54) NOVEL SUBSTITUTED (THIO)UREAS AND THEIR USE AS INSECTICIDES

(71) We, NIHON TOKUSHU NOYAKU SEIZO K.K., a body corporate, organised under the laws of Japan, of No. 8, 3-chome, Nihonbashi Muromachi, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:

The present invention relates to certain new substituted (thio)ureas, to a process for their preparation and to their use as arthropodocides, especially as insecticides.

It is known from *Chemical Abstracts* Vol. 70, No. 21, 96687y, (1969) that N-benzoyl-N'-substituted-benzothiazol-2-yl thioureas of the general formula



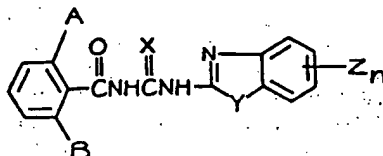
(IV),

in which

R represents hydrogen, methyl or chlorine, can be used as the starting materials for producing benzothiazolylguanidines having Tubercle bacillus-inhibiting, antibacterial and antimycotic activities.

It is also known that most of the damage to crops caused by insects occurs when the latter are in their larval stage. However, it has also been observed that insect pests have developed a resistance to the conventional organophosphorus and carbamate insecticides, which have been employed in large quantities over a long period.

The present invention now provides substituted (thio)-urea compounds of the general formula



(I)

in which

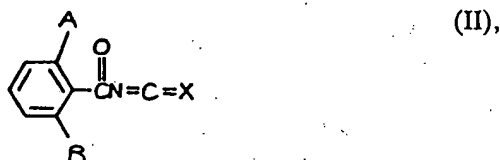
- A represents halogen,  
 B represents hydrogen or halogen,  
 X represents oxygen or sulphur,  
 Y represents oxygen or sulphur,

Z represents halogen and

$n$  is 1 or 2, the Z atoms being identical or different when  $n$  is 2.

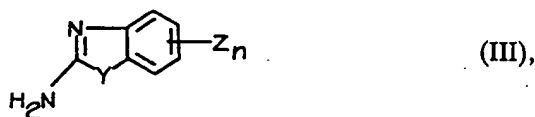
The compounds of the formula (I) have been found to exhibit excellent insecticidal activity, especially against the larvae of insect pests.

5 The present invention also provides a process for the preparation of a compound of the formula (I), in which a benzoyl iso(thio)cyanate of the general formula 5



in which

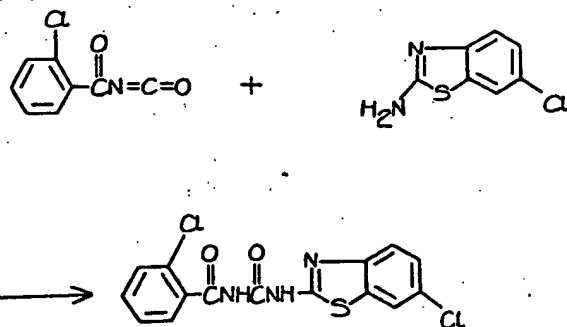
15 A, B and X have the meanings stated above, is reacted with a 2-amino-15  
halogenobenzothiazole or 2-amino-halogenobenzoxazole of the general formula



in which

Y, Z and  $n$  have the meanings stated above.

25 If 2-amino-6-chlorobenzothiazole and 2-chlorobenzoyl isocyanate are used as starting materials, the course of the process according to the present invention can be illustrated by the following equation: 25



45 Examples of the benzoyl isocyanates or benzoyl isothiocyanates of the formula (II), to be used as starting materials, are 2-chlorobenzoyl isocyanate, 2-fluorobenzoyl isocyanate, 2-chlorobenzoyl isothiocyanate, 2-fluoro-benzoyl isothiocyanate, 2,6-dichlorobenzoyl isocyanate, 2,6-difluorobenzoyl isocyanate, and 2,6-difluorobenzoyl isothiocyanate. 45

50 Examples of the 2-amino-halogenobenzothiazoles or 2-amino-halogenobenzoxazoles of the formula (III), also to be used as starting materials, are 2-amino-6-chlorobenzothiazole, 2-amino-6-fluorobenzothiazole, 2-amino-5-chlorobenzoxazole, 2-amino-5-chlorobenzothiazole, 2-amino-5,6-dichlorobenzothiazole, and 2-amino-4,6-dichlorobenzothiazole. 50

55 The process of the present invention is carried out preferably using a solvent or diluent. Examples of such solvents or diluents are water and inert organic solvents selected from aliphatic, alicyclic and aromatic hydrocarbons (which optionally may be chlorinated), such as hexane, cyclohexane, petroleum ether, ligroin, benzene, toluene, xylene, methylene chloride, chloroform, carbon tetrachloride, ethylene chloride, trichloroethylene and chlorobenzene; ethers, such as diethyl ether, methyl ethyl ether, diisopropyl ether, dibutyl ether, propylene oxide, dioxan and tetrahydrofuran; ketones, such as acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl isobutyl ketone; nitriles, such as acetonitrile, propionitrile and acrylonitrile; alcohols, such as methanol, ethanol, isopropanol, the butanols and ethylene glycol; ethers, such as ethyl acetate and amyl acetate; acid amides such as dimethyl formamide and dimethyl acetamide; sulfones and sulfoxides, such as dimethyl sulfoxide and dimethyl sulfone; and organic bases, such as pyridine. 60

65 The process of the present invention can be performed in a wide temperature range. In general, the process is carried out at a temperature between  $-20^{\circ}\text{C}$  and the boiling point of 65

the mixture, preferably at a temperature of from 0° to 100°C. Furthermore, the reaction is preferably carried out at atmospheric pressure, although it can also be performed under an elevated or reduced pressure.

As already mentioned, the compounds according to the present invention are distinguished by an insecticidal activity. They are therefore active against plant pests, pests harmful to health and pests of stored products and combine a low phytotoxicity with a good action against sucking and biting insects.

For this reason, the compounds according to the invention can be employed successfully as pesticides in plant protection and in the hygiene field and the field of protection of stored products.

The compounds according to the present invention can also be used in the field of veterinary medicine since they are also active against animal parasites, including both endo- and ectoparasites, for example insects and worms.

The active compounds are well tolerated by plants, have a favourable level of toxicity to warm-blooded animals, and can be used for combating arthropod pests, especially insects, which are encountered in agriculture, in forestry, in the protection of stored products and of materials, and in the hygiene field. They are active against normally sensitive and resistant species and against all or some stages of development. The above-mentioned pests include:

- from the order of the *Thysanura*, for example *Lepisma saccharina*;
- from the order of the *Collembola*, for example *Onychiurus armatus*;
- from the order of the *Orthoptera*, for example *Blatta orientalis*, *Periplaneta americana*, *Leucophaea maderae*, *Blattella germanica*, *Acheta domesticus*, *Grylloblatta* spp., *Locusta migratoria migratorioides*, *Melanoplus differentialis* and *Schistocerca gregaria*;
- from the order of the *Dermaptera*, for example *Forficula auricularia*;
- from the order of the *Isoptera*, for example *Reticulitermes* spp.;
- from the order of the *Anoplura*, for example *Phylloxera vastatrix*, *Pemphigus* spp., *Pediculus humanus corporis*, *Haematopinus* spp. and *Linognathus* spp.;
- from the order of the *Mallophaga*, for example *Trichodectes* spp. and *Damalinae* spp.;
- from the order of the *Thysanoptera*, for example *Hercinothrips femoralis* and *Thrips tabaci*;
- from the order of the *Heteroptera* for example *Eurygaster* spp., *Dysdercus intermedius*, *Piesma quadrata*, *Cimex lectularius*, *Rhodnius prolixus* and *Triatoma* spp.;
- from the order of the *Homoptera*, for example *Aleurodes brassicae*, *Bemisia tabaci*, *Trialeurodes vaporariorum*, *Aphis gossypii*, *Brevicoryne brassicae*, *Cryptomyzus ribis*, *Doralis fabae*, *Doralis pomi*, *Eriosoma lanigerum*, *Hyalopterus arundinis*, *Macrosiphum avenae*, *Myzus* spp., *Phorodon humuli*, *Rhopalosiphum padi*, *Empoasca* spp., *Euscelis bilobatus*, *Nephotettix cincticeps*, *Lecanium corni*, *Saissetia oleae*, *Laodelphax striatellus*, *Nilaparvata lugens*, *Aonidiella aurantii*, *Aspidiotus hederae*, *Pseudococcus* spp. and *Psylla* spp.;
- from the order of the *Lepidoptera*, for example *Pectinophora gossypiella*, *Bupalus piniarius*, *Cheimatobia brumata*, *Lithocolletis blancardella*, *Hyponomeuta padella*, *Plutella maculipennis*, *Malacosoma neustria*, *Euproctis chrysorrhoea*, *Lymantria* spp., *Bucculatrix thurberiella*, *Phyllocnistis citrella*, *Agrotis* spp., *Euxoa* spp., *Feltia* spp., *Earias insulana*, *Heliothis* spp., *Laphygma exigua*, *Mamestra brassicae*, *Panolis flammea*, *Prodenia litura*, *Spodoptera* spp., *Trichoplusia ni*, *Carpocapsa pomonella*, *Pieris* spp., *Chilo* spp., *Pyrausta nubilalis*, *Ephestia kuehniella*, *Galleria mellonella*, *Cacoecia podana*, *Capua reticulana*, *Choristoneura fumiferana*, *Clysia ambiguella*, *Homona magnanima* and *Tortrix viridana*;
- from the order of the *Coleoptera*, for example *Anobium punctatum*, *Rhizophora dominica*, *Bruchidius obtectus*, *Acanthoscelides obtectus*, *Hylotrupes bajulus*, *Agelastica alni*, *Leptinotarsa decemlineata*, *Phaedon cochleariae*, *Diabrotica* spp., *Psylliodes chrysocephala*, *Epilachna varivestis*, *Atomaria* spp., *Oryzaephilus surinamensis*, *Anthonomus* spp., *Sitophilus* spp., *Otiorrhynchus sulcatus*, *Cosmopolites sordidus*, *Ceuthorrhynchus assimilis*, *Hypera postica*, *Dermestes* spp., *Trogoderma* spp., *Anthrenus* spp., *Attagenus* spp., *Lyctus* spp., *Meligethes aeneus*, *Ptinus* spp., *Niptus hololeucus*, *Gibbium psyllodes*, *Tribolium* spp., *Tenebrio molitor*, *Agriotes* spp., *Conoderus* spp., *Melolontha melolontha*, *Amphimallon solstitialis* and *Costelytra zealandica*;
- from the order of the *Hymenoptera*, for example *Diprion* spp., *Hoplocampa* spp., *Lasius* spp., *Monomorium pharaonis* and *Vespa* spp.;
- from the order of the *Diptera*, for example *Aedes* spp., *Anopheles* spp., *Culex* spp., *Drosophila melanogaster*, *Musca* spp., *Fannia* spp., *Calliphora erythrocephala*, *Lucilia* spp., *Chrysomya* spp., *Cuterebra* spp., *Gastrophilus* spp., *Hyppobosca* spp., *Stomoxys* spp., *Oestrus* spp., *Hypoderma* spp., *Tabanus* spp., *Tannia* spp., *Bibio hortulanus*, *Oscinella frit*, *Phorbia* spp., *Pegomya hyoscyami*, *Ceratitis capitata*, *Dacus oleae* and *Tipula paludosa*; and
- from the order of the *Siphonaptera*, for example *Xenopsylla cheopis* and *Ceratophyllus*

spp.

The active compounds can be converted into the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, dusting agents, foams, pastes, soluble powders, granules, aerosols, suspension-emulsion concentrates, seed-treatment powders, natural and synthetic materials impregnated with active compound, very fine capsules in polymeric substances, coating compositions for use on seed, and formulations used with burning equipment, such as fumigating cartridges, fumigating cans and fumigating coils, as well as ULV cold mist and warm mist formulations.

These formulations may be produced in known manner, for example by mixing the active compounds with extenders, that is to say liquid or liquefied gaseous or solid diluents or carriers, optionally with the use of surface-active agents, that is to say emulsifying agents and/or dispersing agents and/or foam-forming agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents.

As liquid solvents diluents or carriers, especially solvents, there are suitable in the main, aromatic hydrocarbons, such as xylene, toluene or alkyl naphthalenes, chlorinated aromatic or chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic or alicyclic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, alcohols, such as butanol or glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, or strongly polar solvents, such as dimethylformamide and dimethylsulphoxide, as well as water.

By liquefied gaseous diluents or carriers are meant liquids which would be gaseous at normal temperature and under normal pressure, for example aerosol propellants, such as halogenated hydrocarbons as well as butane, propane, nitrogen and carbon dioxide.

As solid carriers there may be used ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly-dispersed silicic acid, alumina and silicates. As solid carriers for granules there may be used crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks.

As emulsifying and/or foam-forming agents there may be used non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates, alkyl sulphates, aryl sulphonates as well as albumin hydrolysis products. Dispersing agents include, for example, lignin sulphite waste liquors and methyl-cellulose.

Adhesives such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, can be used in the formulations.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs or metal phthalocyanine dyestuffs, and trace nutrients, such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations in general contain from 0.1 to 95 per cent by weight of active compound, preferably from 0.5 to 90 per cent by weight.

The active compounds according to the invention may be used in the form of their formulations of the types that are commercially available or in the use forms prepared from these formulations.

The active compound content of the use forms prepared from the formulations of the types that are commercially available can vary within wide ranges. The active compound concentration of the use forms can be from 0.0001 to 20% by weight of active compound, preferably 0.005 to 10% by weight.

The compounds may be employed in a customary manner appropriate for the particular use forms.

In general, 0.03 to 10 kg, preferably 0.3 to 6 kg, of active compound are employed per hectare of soil surface. However, it is possible to use higher or lower amounts and in certain circumstances this may prove necessary.

When used against pests harmful to health and pests of stored products, the active compounds are distinguished by an excellent residual activity on wood and clay as well as a good stability to alkali on limed substrates.

The present invention also provides an arthropodicidal composition containing as active ingredient a compound of the present invention in admixture with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

The present invention also provides a method of combating arthropods, especially

insects, which comprises applying to the arthropods, or to a habitat thereof, a compound of the present invention alone or in the form of a composition containing as active ingredient a compound of the present invention in admixture with a diluent or carrier.

5 The present invention further provides crops protected from damage by arthropods by being grown in areas in which immediately prior to and/or during the time of the growing a compound of the present invention was applied alone or in admixture with a diluent or carrier. 5

It will be seen that the usual methods of providing a harvested crop may be improved by the present invention.

10 Various pesticidal compositions according to this invention are described in the following Examples. The compounds of the present invention are each identified by the number of the corresponding preparative Example. Parts are by weight. 10

*Example (i)*

15 A wettable powder was prepared by pulverizing and mixing 15 parts of compound No. 1, 80 parts of a mixture (1:5) of diatomaceous earth and kaolin, and 5 parts of an emulsifier (a polyoxyethylene alkylphenyl ether). This could be diluted with water to a concentration of 0.05% before application by spraying. 15

20 *Example (ii)* 20

An emulsifiable concentrate was prepared by mixing and stirring 10 parts of compound No. 2, 40 parts of methyl isobutyl ketone, 40 parts of methylnaphthalene and 10 parts of a polyoxyethylene alkylphenyl ether. This could be diluted with water to a concentration of 0.05% before spraying. 25

*Example (iii)* 25

A dusting agent was prepared by pulverizing and mixing 2 parts of compound No. 3 and 98 parts of a mixture (1:3) of talc and clay. This could be applied by scattering.

30 *Example (iv)* 30

A dusting agent was prepared by pulverizing and mixing 1.5 parts of compound No. 4, 0.5 part of isopropyl hydrogen phosphate (PAP), and 98 parts of a mixture (1:3) of talc and clay.

35 *Example (v)* 35

10 parts of compound No. 5, 10 parts of bentonite, 78 parts of a mixture (1:3) of talc and clay, and 2 parts of lignin sulfonate were mixed. 25 parts of water were added to the mixture. The whole was mixed thoroughly and then processed with an extrusion granulator into granules of 20 to 40 mesh, which were dried at 40-50°C.

40 *Example (vi)* 40

95 parts of clay powder having a particle size distribution of 0.2 to 2 mm were placed in a rotary mixer. During rotation, there were sprayed over the particles 5 parts of a solution of compound No. 6 in an organic solvent, thereby wetting them uniformly. Then, drying at 40 to 50°C was effected in order to form granules. 45

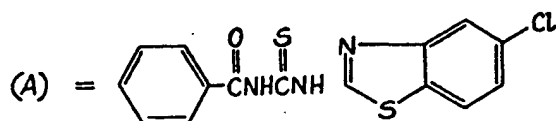
*Example (vii)*

An oil preparation was prepared by mixing and stirring 0.5 part of compound No. 7, 20 parts of a high-boiling aromatic compound and 79.5 parts of kerosine.

50 The insecticidal activity of the compounds of this invention is illustrated by the following biotest Examples. 50

In these Examples, the compounds according to the present invention are each identified by the number (given as brackets) of the corresponding preparative Example, which will be found later in this specification.

55 The known comparison compound is identified as follows: 55



(described in *Chemical Abstracts* Vol. 70, No. 21,96697y (1969))

**Example A**

Test against *Spodoptera litura* larvae

To prepare a suitable preparation of the active compound, 5 parts of the compound, 4 parts of a 1:5 mixture of diatomaceous earth and kaolin and 1 part of a polyoxyethylene alkyl-phenyl ether were ground and mixed together to give a wettable powder. The mixture was diluted with water to the prescribed concentration.

Sweet-potato leaves were dipped into the preparation of the active compound diluted to the prescribed concentration, dried and put in a Petri dish of 9 cm in diameter. 10 *Spodoptera litura* larvae (3rd instar) were placed in the dish. The dish was kept in a constant-temperature room at 28°C. After 5 days, the number of dead larvae was counted and the killing rate was calculated.

TABLE A

Test result on <i>Spodoptera litura</i> larvae					
Active compound the active compound (in ppm) of:					
Killing rate (%) at a concentration of:					
	1000	300	100	30	10
( 1 )	100	100	100	100	100
( 2 )	100	100	100	100	100
( 3 )	100	100	100	100	100
( 4 )	100	100	100	100	100
( 5 )	100	100	100	100	-
( 6 )	100	100	100	100	-
( 7 )	100	100	100	100	-
( 8 )	100	100	100	100	-
( 9 )	100	100	100	100	-
(10)	100	100	100	100	-
(11)	100	100	100	100	-
(A)	50	0	0	0	0

**Example B**

Test against *Culex pipiens* larvae

100 ml of a solution of the active compound diluted to the prescribed concentration was added to a deep Petri dish of 9 cm in diameter. 25 *Culex pipiens* larvae (4th instar) were placed in the dish. The dish was kept in a constant-temperature room at 28°C. After 3 days, the number of dead larvae was counted and the killing rate was calculated.

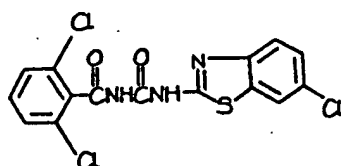
TABLE B

Test result on *Culex pipiens* larvae

5	Active compound	Killing rate (%) at a concentration of the active compound (in ppm) of		5
		1	0.1	
	(3)	100	100	
10	(6)	100	100	10
	(8)	100	100	
15	(9)	100	100	15
	(A)	50	0	

The following preparative Examples illustrate the process of the present invention.

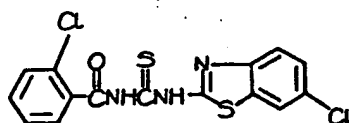
## Example 1



(1)

18.4 g of 2-amino-6-chlorobenzothiazole were dissolved in 450 ml of methyl ethyl ketone and a solution of 21.5 g of 2,6-dichlorobenzoyl isocyanate in 50 ml of methyl ethyl ketone was added dropwise with stirring and cooling. After this addition, the mixture was heated to 50°C and stirred for 3 hours. It was then allowed to cool to below room temperature, the precipitated crystals were filtered off and recrystallized from a mixture of dimethylformamide and ethanol to give 36.7 g of N-(6-chlorobenzothiazol-2-yl)-N'-(2,6-dichlorobenzoyl)urea. Melting point = 300°C. The structure was confirmed by the IR spectrum.

## Example 2



(2)

2.43 g of potassium thiocyanate were dissolved in 60 ml of acetone and 3.48 g of 2-chlorobenzoyl chloride were added while cooling and the mixture was then heated under reflux for 30 minutes. After cooling to below room temperature, the resultant potassium chloride was removed by filtration and 3.68 g of 2-amino-6-chlorobenzothiazole were added to the filtrate, which was then heated at 50°C for 4 hours. After the reaction, acetone was evaporated off under reduced pressure and the residue was recrystallized from a mixture of tetrahydrofuran and ethyl alcohol to give 4.4 g of N-(6-chlorobenzothiazol-2-yl)-N'-(2-chlorobenzoyl)thiourea. M.pt. = 229 - 230°C.

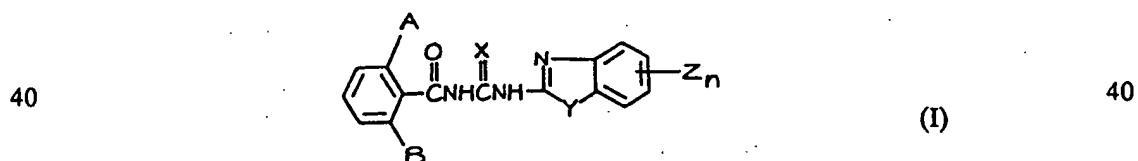
The compounds disclosed in the following table were prepared by analogous procedures. The structures of the compounds of Examples 4 to 9 were confirmed by the infra-red spectra.

TABLE 1

5								5
							(I)	
10	Example No.	A	B	X	Y	Z <sub>n</sub>	Melting point	10
	3	Cl	H	O	S	6-Cl	290-295°C	
15	4	Cl	H	O	S	6-F	300°C	15
	5	Cl	H	O	S	5,6-Cl <sub>2</sub>	300°C	
	6	Cl	Cl	O	S	5-Cl	300°C	
20	7	Cl	Cl	O	S	6-F	300°C	20
	8	Cl	Cl	O	S	4,6-Cl <sub>2</sub>	300°C	
25	9	F	F	O	S	6-Cl	300°C	25
	10	F	F	S	S	6-Cl	225°C - 226°C	
	11	F	H	S	S	6-F	185°C - 188°C	
30	12	Cl	H	S	O	5-Cl	201°C - 202°C	30

## WHAT WE CLAIM IS:

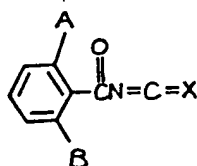
- 35 1. Substituted (thio)urea compounds of the general formula



45 in which

- 45 A represents halogen,
- B represents hydrogen or halogen,
- 50 X represents oxygen or sulphur,
- Y represents oxygen or sulphur,
- 55 Z represents halogen and
- n is 1 or 2, the Z atoms being identical or different when n is 2.
2. The compound according to claim 1 that is disclosed in any one of Examples 1 to 12.
- 60 3. A process for the preparation of a compound according to claim 1, in which a benzoyl iso(thio)cyanate of the general formula

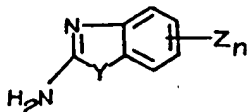




(II),

in which

A, B and X have the meanings stated in claim 1, is reacted with a 2-amino-halogenobenzothiazole or 2-amino-halogenobenzoxazole of the general formula



(III),

in which

Y, Z and  $n$  have the meanings stated in claim 1.

4. A process according to claim 3, in which the reaction is effected in an inert solvent or diluent.

5. A process according to claim 3 or 4, in which the reaction is effected at from  $-20^{\circ}\text{C}$  to the boiling point of the reaction mixture.

6. A process according to claim 5, in which the reaction is effected at from  $0^{\circ}$  to  $100^{\circ}\text{C}$ .

7. A process according to any of claims 3 to 6, in which the reactants (II) and (III) are each hereinbefore specifically mentioned.

8. A process for the preparation of a compound according to claim 1, substantially as described in Example 1 or 2.

9. Compounds according to claim 1 whenever prepared by a process according to any of claims 3 to 8.

10. An arthropodicidal composition containing as active ingredient a compound according to claim 1, 2 or 9 in admixture with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

11. A composition according to claim 10 containing from 0.1 to 95% of the active compound, by weight.

12. A method of combating arthropods which comprises applying to the arthropods, or to a habitat thereof, a compound according to claim 1, 2 or 9 alone or in the form of a composition containing as active ingredient a compound according to claim 1, 2 or 9, in admixture with a diluent or carrier.

13. A method according to claim 12 in which a composition is used containing from 0.0001 to 20% of the active compound, by weight.

14. A method according to claim 13 in which a composition is used containing from 0.005 to 10% of the active compound, by weight.

15. A method according to claim 12, 13 or 14 in which the active compound is applied to an area of agriculture in an amount of 0.03 to 10 kg per hectare.

16. A method according to claim 15 in which the active compound is applied to an area of agriculture in an amount of 0.3 to 6 kg per hectare.

17. A method according to any of claims 12 to 16, in which the arthropods are insects.

18. Crops protected from damage by arthropods by being grown in areas in which immediately prior to and/or during the time of the growing a compound according to claim 1, 2 or 9 was applied alone or in admixture with a diluent or carrier.

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